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SYNTHESIS AND CHARACTERIZATION OF IRON(2+) AND RUTHENIUM(2+) DIIMINO-, DIAMINO- AND DIAMIDO-DIPHOSPHINE COMPLEXES. X-RAY CRYSTAL STRUCTURE OF *TRANS*-$RuCl_2(P_2N_2C_2H_4)\cdot CHCl_3$

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Abstract—The interaction of $Ru(OAc)_2(Ph_3P)_2$ with one equivalent of *N,N'*-bis[*o*-(diphenylphosphino)benzylidene]ethylenediamine ($P_2N_2C_2$) in refluxing dichloromethane gave *trans*-$Ru(OAc)_2(P_2N_2C_2)\cdot 2H_2O$ (**I**) in moderate yield (63%); in refluxing-toluene, it gave a red solid which upon recrystallization in $CHCl_3$ gave *trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$ (**II**) in good yield (92%). Compound **II** could also be prepared in good yield (85%) via the interaction of $RuCl_2(DMSO)_4$ with one equivalent of $P_2N_2C_2$ in refluxing toluene. The interaction of $RuCl_2(DMSO)_4$ with one equivalent of *N,N'*-bis[*o*-(diphenylphosphino) benzylidene]-1,3-diaminopropane ($P_2N_2C_3$), *N,N'*-bis[*o*-(diphenylphosphino)benzyl] ethylenediamine ($P_2N_2C_2H_4$) and *N,N'*-bis[*o*-(diphenylphosphino)benzamido]ethane ($P_2N_2C_2$-amide) in refluxing toluene gave *trans*-$RuCl_2(P_2N_2C_3)$ (**III**), *trans*-$RuCl_2(P_2N_2C_2H_4)$ (**IV**) and *trans*-$RuCl_2(P_2N_2C_2$-amide) (**V**) in good yield, respectively. The interaction of $Fe(ClO_4)_2\cdot 6H_2O$ with one equivalent of $P_2N_2C_2$ and $P_2N_2C_2H_4$ in refluxing acetonitrile gave *trans*-$[Fe(P_2N_2C_2)(CH_3CN)_2](ClO_4)_2$ (**VI**) and *trans*-$[Fe(P_2N_2C_2H_4)(CH_3CN)_2](ClO_4)_2$ (**VII**), respectively. Interaction of $FeCl_2\cdot 4H_2O$ with one equivalent of *N,N'*-bis[*o*-(diphenylphosphino)benzylidene]-1,6-diaminohexane ($P_2N_2C_6$) in refluxing gave *trans*-$FeCl_2(P_2N_2C_6)$ (**VIII**). Complexes **I**–**VIII** have been fully characterized by analytical and spectroscopic methods. The structure of **IV** has been established by an X-ray diffraction study. Compound **II** could be reduced to compound **IV** with $NaBH_4$ in ethanol and oxidized to **V** with aqueous H_2O_2 acetonitrile. Catalytic studies showed that both **II** and **IV** were effected catalysts for the hydrogenation of acrylic acid to propionic acid.

The compounds $Ru(OAc)_2(Ph_3P)_2$ and $RuCl_2(DMSO)_4$ are very versatile reagents. They provide a very good entry to ruthenium(2+) complexes. Since their preparation, a large number of ruthenium carboxylate and chloride complexes have been synthesized.[1–3] Ruthenium–phosphine complexes have been shown to display various cata-

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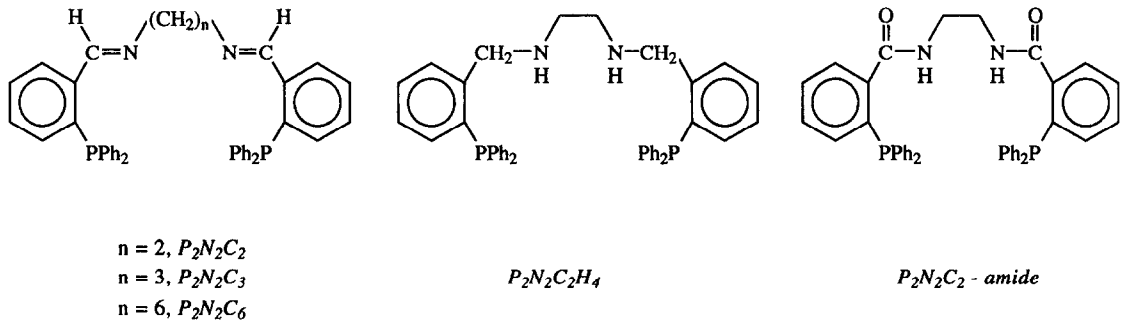
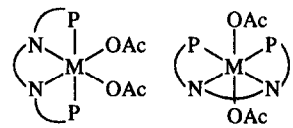
lytic properties,[4] particularly those with chiral chelating diphosphine ligands.[5] Chelating, multidentate phosphate ligands offer several advantages over monodentate phosphines containing similar phosphino groups. They can provide better control over the coordination number and stereochemistry of the resulting complexes, increase basicity at the metal centres and slow down intra- and intermolecular exchange processes.[6] The coordination chemistry of *N,N'*-bis[*o*-(diphenylphosphino) benzylidene]ethylenediamine ($P_2N_2C_2$), a polydentate ligand containing both nitrogen and phosphorus donor functional groups, has been examined recently and shows that the ligand can serve as a bi-, tri- and tetra-dentate ligand depending on the reaction condition.[7–10] It is likely that ruthenium complexes containing the $P_2N_2C_2$ ligand may display some interesting structural, chemical and catalytic properties that are not observed in other chelating phosphine complexes. Recently, we have communicated the preparation and X-ray crystal structure of *trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$.[11] In this paper, we report the detailed syntheses and characterization of ruthenium(2+) and iron(2+) diimino-, diamino- and diamido-diphosphine complexes. The catalytic hydrogenation activity of the ruthenium(2+) diimimo- and diamino-diphosphine complexes is also presented.



RESULTS AND DISCUSSION

Preparation of ruthenium(2+) *complexes*

(*i*) *Trans*-$Ru(OAc)_2(P_2N_2C_2)\cdot 2H_2O$ (**I**). When $Ru(OAc)_2(Ph_3P)_2$ was treated with one equivalent of $P_2N_2C_2$ in refluxing CH_2Cl_2 for 16 h, work-up gave red crystals of stoichiometry $[Ru(CH_2COO)_2(P_2N_2C_2)]\cdot 2H_2O$ (**I**) in moderate yield (63%) after recrystallization from an acetone/diethyl ether mixture. Compound **I** exhibited absorption at 1562vs and 1380s cm^{-1} in the IR spectrum and a singlet at δ 1.07 in the ^1H NMR spectrum for the acetate groups. Other than the phenyl and water protons, the ^1H NMR spectrum of **I** also exhibited a multiplet and a singlet of relative intensity 2.4 at δ 8.97 and 4.59 for the protons of the —C*H*=N— and —NCH_2CH_2N— groups, respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **I** exhibited a singlet at δ 48.6 indicating that the two phosphino groups of the $P_2N_2C_2$ ligand were coordinated and equivalent. The IR and ^1H NMR data indicated that the two acetate groups were monodentate and equivalent. This ruled out the salt formation $[Ru(OAc)(P_2N_2C_2)][OAc]$. There are two possible isomers for **I**. These are the *cis*- and *trans*-isomers shown.



The available spectroscopic data could not distinguish between the two isomers. However, since both $RuCl_2(P_2N_2C_2)$[11] and $Ru(OAc)_2(P_2N_2C_2H_4)$[12] complexes adopt a *trans*-configuration, a *trans*-configuration was also assigned to **I**.

(*ii*) *Trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$ (**II**). When the above reaction was carried out in refluxing toluene for 16 h, work-up gave a red solid whose IR and ^1H NMR spectra showed the absence of the acetate groups. The red solid exhibited a very complex ^1H NMR spectrum; however, its $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibited only a singlet at δ 3.8. Attempts to obtain an analytically pure sample of the red solid for analysis were unsuccessful. When the red solid was recrystallized from a $CHCl_3$/hexane mixture, dark red crystals of stoichiometry $RuCl_2(P_2N_2C_2)\cdot 2H_2O$ (**II**) were obtained in high yield (92%). This showed that the red solid reacted with $CHCl_3$ to give **II**, and the chloro ligands of **II** originated from $CHCl_3$. The red solid was probably a doubly cyclometallated product formed by elimination of two

moles of CH_3COOH and reacted with $CHCl_3$ to give **II**.

The IR and ^1H NMR spectra of **II** did not exhibit any absorptions due to acetate groups. Compound **II** exhibited an IR band at 1628 cm^{-1} characteristic of ν(C=N) for the imino groups. Other than the phenyl and water protons, the ^1H NMR spectrum of **II** also exhibited a multiplet and a singlet of relative intensities 2:4 at δ 8.99 and 4.35 for the protons of the —C*H*=N— and —NCH_2CH_2N— groups, respectively. The ^{31}P-{H} NMR spectrum of **II** exhibited a singlet at δ 46.1 indicating that the two phosphino groups of the $P_2N_2C_2$ ligand were coordinated and equivalent. The available spectroscopic data again could not distinguish between the *cis*- and *trans*-configuration of **II**. The structure of **II** was established by X-ray crystallography to be the *trans*-configuration.[11] Compound **II** could also be obtained in high yield (85%) via the interaction of $RuCl_2(DMSO)_4$ with one equivalent of $P_2N_2C_2$ in refluxing toluene.

(*iii*) *Trans*-$RuCl_2(P_2N_2C_3)$ (**III**). The interaction of $RuCl_2(DMSO)_4$ with equimolar $P_2N_2C_3$ generated *in situ* in refluxing ethanol gave red crystals of stoichiometry $RuCl_2(P_2N_2C_3)$ (**III**) in moderate yield (67%). Compound **III** exhibited an IR band at 1631 cm^{-1} characteristic of ν(C=N) for the imino groups. In addition to the phenyl protons, the ^1H NMR spectrum of **III** exhibited a multiplet, a triplet (J = 7.6 Hz) and a doublet (J = 8.4 Hz) of relative intensities 2:4:2 at δ 3.65, 4.23 and 9.02 for the protons of —NCH_2CH_2CH_2N—, —NCH_2 CH_2CH_2N— and —C*H*=N— groups, respectively. The ^{31}P-{^1H} NMR spectrum of **III** exhibited a singlet at δ 64.8. The spectroscopic data indicated that the two chloro ligands were equivalent and the two phosphino groups of the $P_2N_2C_3$ ligands were coordinated and equivalent. The structure of **III** is expected to be similar to that of **II**, thus, a *trans*-configuration is assigned to **III**.

(*iv*) *Trans*-$RuCl_2(P_2N_2C_2H_4)$ (**IV**). The interaction of $RuCl_2(DMSO)_4$ with equimolar $P_2N_2C_2H_4$ in refluxing toluene for 48 h gave yellow crystals of stoichiometry $RuCl_2(P_2N_2C_2H_4)$ (**IV**) in moderate yield (70%). Compound **IV** exhibited an IR band at 3200 cm^{-1} characteristic of ν(NH) for the amino groups. Other than the phenyl protons, the ^1H NMR spectrum of **IV** also exhibited a multiplet of relative intensity 2 at δ 3.07 for the protons of the —N*H*— groups, two multiplets of relative intensities 2:2 at δ 4.57 and 4.84 for the protons of the PhCH_2— groups, and two multiplets of relative intensities 2:2 at δ 3.32 and 3.78 for the protons of the —NCH_2CH_2N— group. The ^{31}P-{^1H} NMR spectrum of **IV** exhibited a singlet at δ 45.9 indicating that the two chloro ligands were equivalent and the two phosphino groups of the $P_2N_2C_2H_4$ ligand were coordinated and equivalent. Since the available spectroscopic data could not distinguish between the *cis*- and *trans*-isomers, an X-ray diffraction study was performed to establish the structure unequivocally. Crystals of **IV** suitable for X-ray diffraction study were grown from $CHCl_3$/diethyl ether as a solvate of stoichiometry **IV** · $CHCl_3$. A perspective drawing of **IV** is shown in Fig. 1, and selected bond lengths and bond angles are given in the caption. All bond lengths and angles are normal.

The solid-state structure of **IV** is consistent with the spectroscopic data and reveals a *trans*-configuration for the octahedral complex. The structure shows that the two chloro ligands are mutually *trans* to each other and the $P_2N_2C_2H_4$ ligand acts as a tetradentate ligand with the two phosphino groups *cis* to each other.

(*v*) *Trans*-$RuCl_2(P_2N_2C_2$-amide) (**V**). The interaction of $RuCl_2(DMSO)_4$ with equimolar $P_2N_2C_2$-amide in refluxing toluene for 10 h gave an orange solid of stoichiometry $RuCl_2(P_2N_2C_2$-amide) (**V**) in moderate yield (59%). Compound **V** exhibited IR bands at 3327 and 1624 cm^{-1} characteristic of ν(—CO*NH*—) and ν(—*CO*NH—) of the amide groups, respectively. The ^{13}C-{^1H} NMR spectrum of **V** exhibited a singlet at δ 171.4 for the carbons of the —*C*ONH— groups. Other than the phenyl protons, the ^1H NMR spectrum of **V** also exhibited two singlets of relative intensities 4:2 at δ 4.25 and 8.89 for the protons of the —NCH_2CH_2N— and —CON*H*— groups, respectively. The ^{31}P-{^1H} NMR spectrum of **V** exhibited a singlet at δ 48.1 indicating that the two phosphino groups were coordinated and equivalent. The structure of **V** should be similar to that of **II** and **IV**, thus, a *trans*-configuration was also assigned to **V**.

Preparation of iron(2+) complexes

(*i*) *Trans*-$[Fe(P_2N_2C_2)(CH_3CN)_2](ClO_4)_2$ (**VI**). The interaction of $Fe(ClO_4)_2 \cdot 6H_2O$ with equimolar $P_2N_2C_2$ in refluxing acetonitrile gave deep red crystals of stoichiometry $[Fe(P_2N_2C_2)\ (CH_2CN)_2]$ $(ClO_4)_2$ (**VI**) in high yield (87%). Compound **VI** exhibited IR bands at 2480 cm^{-1} characteristic of ν(C≡N) for the acetonitrile ligands; at 1625 cm^{-1} characteristic of ν(C=N) for the imino groups; and at 1030 cm^{-1} characteristic of ν(Cl—O) for the perchlorate anions. Other than the phenyl protons, the ^1H NMR spectrum of **VI** exhibited a singlet and a doublet of relative intensity 4:2 at δ 4.41 and 9.50 for the protons of the —HCH_2CH_2N— and —C*H*=N— groups, respectively. The ^1H NMR spectrum also exhibited a singlet of relative inten-

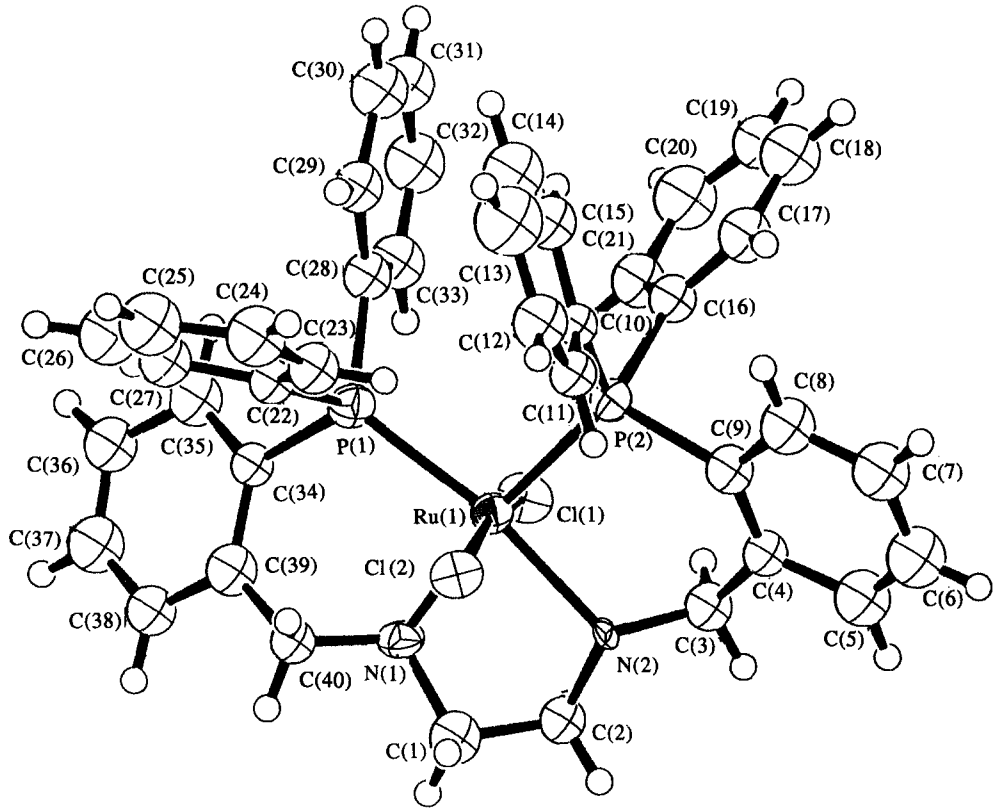


Fig. 1. A perspective view of the structure of *trans*-$RuCl_2(P_2N_2H_4)$, **IV**. Selected bond length (Å) and angles (°): Ru(1)—P(1), 2.303(5); Ru(1)—P(2), 2.303(6); Ru(1)—N(1), 2.17(1); Ru(1)—N(2), 2.16(1); Ru(1)—Cl(1), 2.443(5); Ru(1)—Cl(2), 2.409(5); N(1)—C(40), 1.48(2); N(1)—C(1), 1.50(2); N(2)—C(3), 1.46(2); N(2)—C(2), 1.49(2); Cl(1)—Ru(1)—Cl(2), 165.4(2); P(1)—Ru(1)—P(2), 100.9(2); N(1)—Ru(1)—N(2), 81.0(5); P(1)—Ru(1)—N(1), 89.2(4); P(2)—Ru(1)—N(2), 88.9(4); N(1)—C(40)—C(39), 111(2); N(2)—C(3)—C(4), 111(2); C(1)—N(1)—C(40), 112(1); C(2)—N(2)—C(3), 2113(1).

sity 6 at δ 1.83 for the two coordinated acetonitrile ligands, indicating that the two acetonitrile ligands were equivalent. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **VI** exhibited a singlet at δ 53.6 indicating that the two phosphino groups of the $P_2N_2C_2$ ligand were coordinated and equivalent. The available spectroscopic data could not distinguish between the *cis*- and *trans*-isomers. The structure of **VI** was established by an X-ray diffraction study to be the *trans*-isomer[13] where the two acetonitrile ligands were mutually *trans* to each other and the $P_2N_2C_2$ ligand acted as a tetradentate ligand with the two phosphino group *cis* to each other.

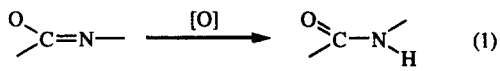
(*ii*) *Trans*-$[Fe(P_2N_2C_2H_4)(CH_3CN)_2](ClO_4)_2$ (**VII**). The interaction of $Fe(ClO_4)_2 \cdot 6H_2O$ with equimolar $P_2N_2C_2H_4$ in refluxing acetonitrile gave orange red crystals of stoichiometry $[Fe(P_2N_2C_2H_4)(CH_3CN)_2](ClO_4)_2$ (**VII**) in moderate yield (61%). Compound **VII** exhibited IR bands at 3403 cm^{-1} characteristic of ν(NH) for the amino groups; at 2476 cm^{-1} characteristic of $\nu(C{\equiv}N)$ for the acetonitrile ligands; and at 1031 cm^{-1} characteristic of ν(Cl—O) for the perchlorate anions. Other than the phenyl protons, the ^1H NMR spectrum of **VII** exhibited a multiplet of relative intensity 2 at δ 3.42 for the —N*H*— protons; two multiplets of relative intensities 2:2 at δ 3.67 and 4.12, respectively, for the $—NCH_2CH_2N—$ protons; and two multiplets of relative intensities 2:2 at δ 4.93 and 5.02, respectively, for the $pHCH_2$-protons. The ^1H NMR spectrum also exhibited a singlet of relative intensity 6 at δ 1.94 for the protons of the two coordinated acetonitrile ligands, indicating that the two acetonitrile ligands were equivalent. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **VII** exhibited a singlet at δ 51.4 indicating the two phosphino groups of the ligand were coordinated and equivalent. The structure of **VII** should be similar to that of **VI**, thus, a *trans*-configuration was assigned to **VII**.

(*iii*) *Trans*-$FeCl_2(P_2N_2C_6)$ (**VIII**). The interaction of $FeCl_2 \cdot 5H_2O$ with equimolar $P_2N_2C_6$ in refluxing ethanol gave yellow crystals of stoi-

chiometry $FeCl_2(P_2N_2C_6)$ (**VIII**) in good yield (73%). Compound **VIII** exhibited an IR band at 1620 cm^{-1} characteristic of ν(C=N) for the imino groups. Other than the phenyl protons and the hexamethylene protons, the ^1H NMR spectrum of **VIII** also exhibited a doublet (J = 5.4 Hz) at δ 9.24 for the —C*H*=N— protons. The ^{31}P-{^1H} NMR spectrum of **VIII** exhibited a singlet at δ 52.1 indicating the two phosphino groups of the ligand were coordinated and equivalent. The structure of **VIII** should be similar to that of **II** and **VI**, thus, a *trans*-configuration was also assigned to **VIII**.

Redox reactions of **II**

(*i*) *Oxidation.* Interaction of **II** with excess aqueous H_2O_2 in acetonitrile gave a yellow crystalline solid in moderate yield (59%). The IR, LRMS, ^1H and ^{31}P-{^1H} NMR spectra of the yellow crystalline solid were identical to those of an authentic sample of **V**. Oxidation of imine to amide as shown in eq. (1) is a rather difficult process.



(1)

The ease of oxidizing **II** to **V** demonstrates that imines could be activated via metal binding and easily oxidized to the corresponding amide. A plausible mechanism for the oxidation of **II** to **V** is shown in Scheme 1. The ruthenium centre of **II** is first oxidized to an oxo-ruthenium species, H_2O is then added to the imino function of the oxidized species to generate the α-hydroxyamino group. Finally, oxygen transfer from the metal centre rapidly oxidizes the α-hydroxyamine moiety to amide with concomittant regeneration of the ruthenium(2+) species. A similar mechanism has been proposed recently for the metal-assisted oxidation of imine to amide.[14]

(*ii*) *Reduction.* Interaction of **II** with excess $NaBH_4$ in ethanol gave an orange crystalline solid in good yield (74%). The IR, LRMS, ^1H and ^{31}P-{^1H} NMR spectra of the orange crystals were identical to those of an authentic sample of **IV**. The reduction was probably via the dissociation of the imino group, followed by rapid reduction of the uncoordinated imino moiety to amine.

Catalytic studies

The catalytic activity of *trans*-$RuCl_2$ $(P_2N_2C_2)\cdot 2H_2O$ for the hydrogenation of acrylic acid to propionic acid in a number of solvents has been examined. The results, shown in Table 1, showed a dramatic solvent effect on the hydrogenation reaction. At an initial hydrogen pressure of 3.0 MPa, a temperature of 60°C, a catalyst/olefin molar ratio of 1:300, and a reaction time of 1.5 h, >99.5% conversion of acrylic acid to propionic acid was observed when the reaction was carried out in methanol; whereas, if the reaction was carried out in $CHCl_3$ under the same conditions, the observed conversion was only 1.6%.

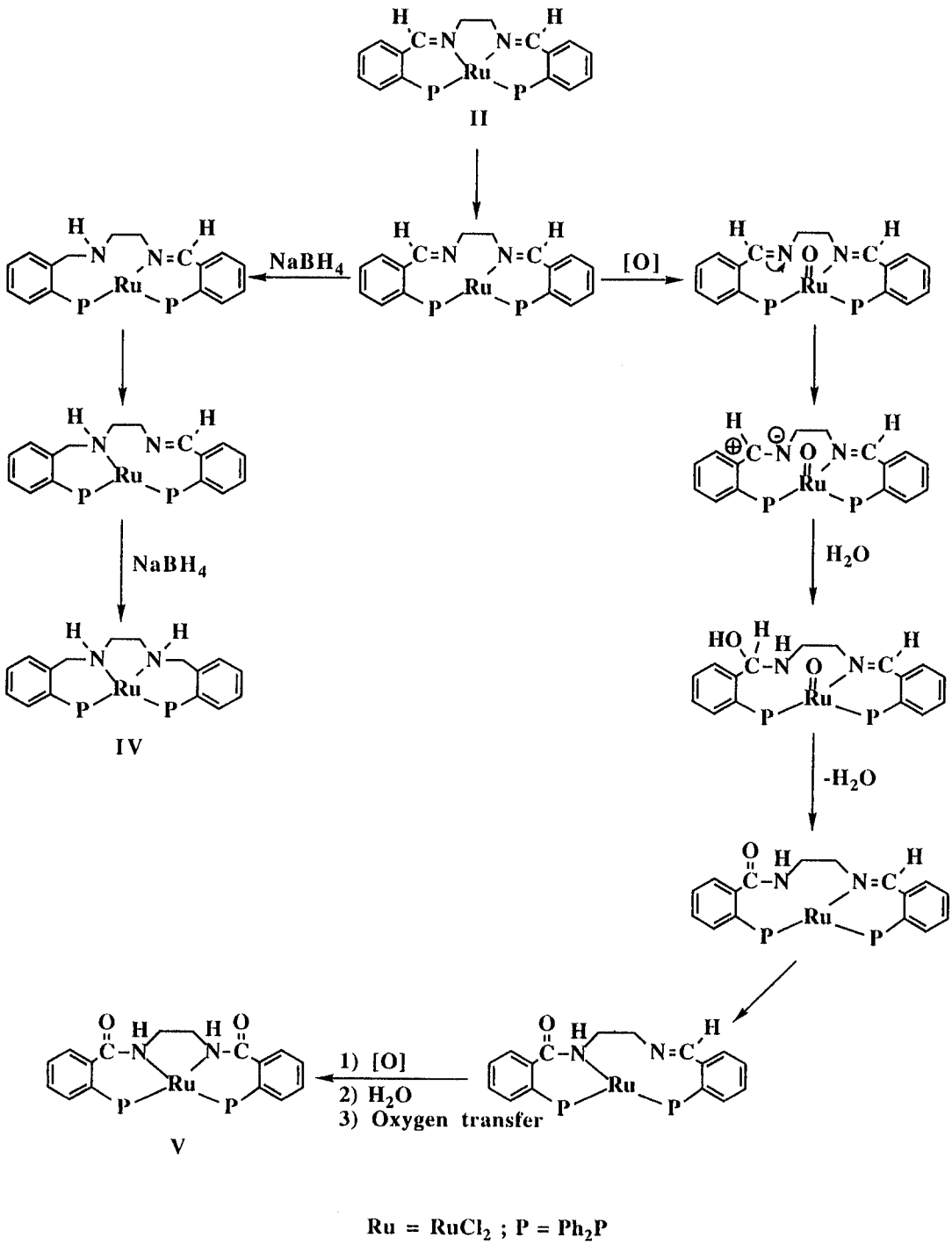
The catalytic activity of a number of ruthenium complexes for the hydrogenation of acrylic and in methanol has also been examined. The results, given in Table 2, demonstrated that ruthenium $P_2N_2C_2$ and $P_2N_2C_2H_4$ complexes were capable of catalysing the hydrogenation of acrylic acid to propionic acid. The results further showed that ruthenium complexes with $P_2N_2C_2H_4$ ligand had a higher activity than the corresponding $P_2N_2C_2$ complexes; and the complexes with chloro ligands had a higher activity than the corresponding complexes with acetate ligands. The above results suggested the possible involvement of a cationic species in the catalytic cycle.

EXPERIMENTAL

Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. IR spectra (KBr pellets) were recorded either on a Hitachi 270-30 IR spectrometer or on a Bio-Rad FTS-45 spectrometer; data are given in cm^{-1}. NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts of ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Chemical shifts of ^1H and ^{13}C NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS = δ 0.00. Low-resolution mass spectra (LRMS) were obtained from the Mass Spectrometry Service, the University of Hong Kong, on a Finnigan MAT 95 spectrometer in FAB (positive) operation mode and are reported as m/z.

All operations were carried out under nitrogen or *in vacuo*. All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled and deaerated prior to use. Catalytic experiments were carried out in a 200-cm^3 stainless autoclave (model GCF-0.2; made in China) with a glass liner. Melting points were taken in sealed capillaries and are uncorrected.

$RuCl_3\cdot 3H_2O$ was purchased from Aldrich and used without further purification $RuCl_2(DMSO)_4$,[15] $Ru(OAc)_2(Ph_3P)_2$,[16] *trans*-$Ru(OAc)_2(P_2N_2C_2H_4)$,[12] $P_2N_2C_2$[9] and $P_2N_2C_2H_4$[9] were prepared according to literature methods.



Scheme 1. Proposed mechanisms for the redox reactions of **II**.

Preparation of ligands

(*i*) $P_2N_2C_2$-amide. The method employed was a modification of the procedure reported by Trost *et al.*[17] A solution of *o*-(diphenylphosphino)benzoic acid (1.9 g, 6.2 mmol), 4-dimethylaminopyridine (0.04 g, 0.3 mmol) and 1,3-dicyclohexylcarbodiimide (1.40 g, 6.8 mmol) in CH_2Cl_2 (30 cm^3) was stirred for an hour. Then a solution of freshly distilled ethylenediamine (0.17 g, 2.7 mmol) in CH_2Cl_2 (10 cm^3) was gradually added to the stirring via a pressurized dropping funnel. The reaction mixture was stirred for 24 h at room temperature, and then filtered through Celite to remove dicyclohexylurea. The filter cake was washed twice with dichloromethane (2×10 cm^3). The solvent of the combined

Table 1. Effect of solvents on the hydrogenation of acrylic acid

Solvent	% Conversion of acrylic acid
Acetone	25.4
Tetrahydrofuran	9.6
Toluene	21.9
Ethanol	45.1
Methanol	>99.5
Dichloromethane	79.8
Chloroform	1.6

Reaction conditions: catalyst, *trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$, 0.05 mmol; acrylic acid, 15 mmol; molar ratio of catalyst/olefin, 1:300; volume of solvents, 30 cm^3; initial hydrogen pressure at room temperature, 3.0 MPa; reaction temperature, 60°C; reaction time, 1.5 h.

filtrate was removed *in vacuo* and the residue was chromatographed on a silica gel column (2 × 15 cm) with 1:2 ethyl acetate/hexane mixture. The eluent was concentrated to *ca* 10 cm^3 and diethyl ether added until the solution turned cloudy. The resulting mixture was cooled to −20°C to afford $P_2N_2C_2$-amide as white crystals. Yield: 1.25 g, 73%; m.p. 139–141°C. Found: C, 75.3; H, 5.4; N, 4.4. Calc. for $C_{40}H_{34}O_2N_2P_2$: C, 75.5; H, 5.3; N, 4.4%. IR (cm^{-1}, in KBr): 3289s(br), 3050w, 1647vs, 1548vs, 1490s, 1437m, 1305vs, 1180s, 1112m, 747vs, 694vs, 503w. ^{31}P-{^1H} NMR ($CDCl_3$): δ −7.85 (s). ^1H NMR ($CDCl_3$): δ 3.38 (4H, s, —NCH_2CH_2N—), 6.63 (2H, s, br, —N*H*—), 6.93–7.61 (28H, m, pH*H*). ^{13}C-{^1H} NMR ($CDCl_3$): δ 40.3 (s, —N*C*H_2*C*H_2N—), 127.0–134.8 (m, Ph-*C*), 167.6 (s, —*C*ONH—). LRMS (FAB: +ve) *m/z*: 637 [M+1].

(*ii*) $P_2N_2C_6$. The method employed was a modification of the procedures reported by Rauchfuss and co-workers.[9] A solution of *o*-(diphenylphosphino)benzaldehyde (5.0 g, 17.2 mmol), 1,6-hexamethylenediamine (1.0 g, 8.6 mmol) and *p*-toluenesulphonic acid monohydrate (0.02 g, 0.1 mmol) in toluene (60 cm^3) was refluxed in a 100-cm^3 round-bottomed flask equipped with a Dean–Stark trap. The solution was allowed to reflux until no more water was collected in the Dean–Stark trap. The solution was cooled, washed with saturated aqueous $NaHCO_3$ solution (2 × 10 cm^3) and dried over $MgSO_4$. The solvent of the toluene solution was removed *in vacuo* to give a pale yellow residue. The residue was redissolved in a minimum amount of $CHCl_3$ and filtered. Hexane was then added to the $CHCl_3$ filtrate until it just turned cloudy. The $CHCl_3$/hexane was cooled to −20°C to give pale yellow crystals, which were filtered and dried *in vacuo*. Yield: 4.66 g, 82%; m.p. 165–167°. Found: C, 80.1; H, 6.4; N, 4.1. Calc. for $C_{44}H_{42}N_2P_2$: C, 80.0; H, 6.4; N, 4.2%. IR (cm^{-1}, in KBr): 3052m, 2925s, 2851w, 1635s, 1440vs, 740s, 721s. ^{31}P-{^1H} NMR ($CDCl_3$): δ −14.7 (s). ^1H NMR ($CDCl_3$): δ 0.95 (4H, m, —NCH_2CH_2 (CH_2)$_2$CH_2CH_2N—), 1.27 (4H, m, —NCH_2C*H* (CH_2)$_2$CH_2CH_2N—), 3.31 (4H, t, J = 7.0 Hz, —NCH_2(CH_2)$_4$C*H*N—), 6.72–7.87 (28H, m, pH-*H*), 8.74 (2H, d, J = 4.9 Hz, —C*H*=N—). ^{13}C-{^1H} NMR ($CDCl_3$): δ 39.9 (s, —NCH_2CH_2 (*C*H_2)$_2$CH_2CH_2N—), 55.0 (s, —NCH_2*C*H_2 (CH_2)$_2$*C*H_2CH_2N—), 59.5 (s, —N*C*H_2 (CH_2)$_4$ *C*H_2N—), 127.4–139.5 (m, Ph-*C*), 160.3 (d, J_{P-C} =

Table 2. Hydrogenation of acrylic acid by various ruthenium complexes[a]

Catalyst	Olefin/catalyst (molar ratio)	Temperature (°C)	Time (h)	Conversion of olefin (%)	Turnover[b] (h^{-1})
$RuCl_3\cdot 3H_2O$	100:1	60	1.5	<1	~1
$RuCl_3\cdot 3H_2O/P_2N_2C_2H_4$[c]	400:1	80	2.0	<1	<3
$Ru(OAc)_2(Ph_3P)_2$	1000:1	100	1.5	41.2	275
I[d]	1000:1	100	1.5	47.0	313
II[d]	1000:1	80	1.5	70.7	471
IX	1500:1	50	1.5	97.0	970
IV	1500:1	50	1.0	99.0	1485

[a] *Reaction conditions*: catalyst, 0.05 mmol; solvent, methanol, 35 cm^3; initial hydrogen pressure at room temperature, 3.0 MPa.

[b] Turnover = mole of propionic acid/mole of catalyst per hour.

[c] $RuCl_3\cdot 3H_2O/P_2N_2C_2H_4$ = 1:1 (molar ratio).

[d] **I**, *trans*-$Ru(OAc)_2(P_2N_2C_2)\cdot 2H_2O$; **II**, *trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$; **IV**, *trans*-$RuCl_2(P_2N_2C_2H_4)$; **IX**, *trans*-$Ru(OAc)_2(P_2N_2C_2H_4)$.

22.0 Hz, —*C*H=N—). LRMS (FAB: +ve) *m/z*: 661 [M+1].

Preparation of ruthenium (2+) complexes

(*i*) *Trans*-$Ru(OAc)_2(P_2N_2C_2)\cdot 2H_2O$ (**I**). A solution of $Ru(OAc)_2(Ph_3P)_2$ (0.37 g, 0.5 mmol) and $P_2N_2C_2$ (0.30 g, 0.5 mmol) in CH_2Cl_2 (15 cm^3) was refluxed for 12 h. A red solution was obtained. The solvent was removed *in vacuo* to give a red residue. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on a silica gel column (2 × 15 cm). A dark red band and a red band were obtained when the column was eluted with CH_2Cl_2/acetone (1 : 1) and methanol solution, respectively. Removal of the solvent from the red band gave a dark red residue. The dark residue was redissolved in a minimum amount of $CHCl_3$. Hexane was added to the $CHCl_3$ solution slowly until it turned cloudy. The $CHCl_3$/hexane mixture was then cooled to −20°C to give dark red crystals, whose IR, ^1H and ^{31}P-$\{^1H\}$ spectra were identical to those of **II** (*vide infra*). Yield: 0.08 g, 20%.

Removal of solvent from the red band gave a red residue, which was redissolved in *ca* 5 cm^3 of acetone. Diethyl ether was added to the acetone solution slowly until it turned cloudy. The acetone/diethyl ether mixture was then cooled to −20°C to give red crystals, which were filtered and dried *in vacuo*. Yield: 0.26 g, 63%, m.p. 216–219°C (dec.). Found: C, 61.3; H, 4.8; N, 3.1. Calc. for $(C_{44}H_{40}O_4N_2P_2Ru)\cdot 2H_2O$: C, 61.5; H, 5.1; N, 3.3%. IR (cm^{-1}, in KBr): 3400s, 3048w, 1608s, 1582vs, 1562vs, 1478w, 1430s, 1380s, 1326w, 1264w, 1182w, 1138w, 1090m, 1020w, 740m, 684m, 508m, 458m. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 48.6 (s). ^1H NMR ($CDCl_3$): δ 8.97 (2H, m, —C*H*=N—), 6.80–7.53 (28H, m, Ph-*H*), 4.59 (4H, s, —NCH_2 CH_2N—), 1.69 (4H, s, H_2O), 1.07 (6H, s, CH_3COO).

(*ii*) *Trans*-$RuCl_2(P_2N_2C_2)\cdot 2H_2O$ (**II**). *Method A.* A solution of $Ru(OAc)_2(Ph_3P)_2$ (0.37 g, 0.5 mmol) and $P_2N_2C_2$ (0.30 g, 0.5 mmol) in toluene (20 cm^3) was refluxed for 16 h to give a red solution. The solvent was removed *in vacuo* to give a dark red residue. The residue was then redissolved in a minimum amount of CH_2Cl_2 and chromatographed on a silica gel column (2 × 15 cm). A dark red band was obtained when the column was eluted with a mixture of CH_2Cl_2/acetone (1 : 1). Removal of solvent from the dark red band gave a dark red residue, which was redissolved in *ca* 10 cm^3 of $CHCl_3$. Hexane was then added to the $CHCl_3$ solution slowly until it just turned cloudy. The $CHCl_3$ hexane mixture was then cooled to −20°C to give dark red crystals, which were filtered and dried *in vacuo*. Yield: 0.36 g, 92%, m.p. 168–171°C (dec.). Found: C, 59.3; H, 4.5; N, 3.3; Cl, 9.0. Calc. for $(C_{40}H_{34}N_2P_2Cl_2Ru)\cdot 2H_2O$: C, 59.1; H, 4.7; N, 3.4; Cl, 8.7%. IR (cm^{-1}, in KBr): 3476br, 3044m, 2916w, 1628m, 1478m, 1428s, 1344w, 1298m, 1264m, 1216w, 1186w, 1156w, 1134w, 1088m, 740s, 686vs, 476m. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 46.1 (s). ^1H NMR ($CDCl_3$): δ 8.99 (2H, m, —C*H*=N—), 6.80–7.60 (28H, m, Ph-*H*), 4.35 (4H, s, —NCH_2 CH_2N—), 1.53 (4H, s, H_2O).

Method B. A suspension of $RuCl_2(DMSO)_4$ (0.24 g, 0.5 mmol) and $P_2N_2C_2$ (0.30 g, 0.5 mmol) in toluene (30 cm^3) was refluxed for 16 h to give a clear dark red solution. The resulting solution was concentrated to *ca* 10 cm^3 and cooled to −20°C to give red solids. The red solids were filtered and recrystallized in a mixture of $CHCl_3$/hexane to give dark red crystals, whose IR, ^1H and ^{31}P-$\{^1H\}$ NMR spectra were identical to those of **II**. Yield: 0.33 g, 85%.

(*iii*) *Trans*-$RuCl_2(P_2N_2C_3)\cdot 2H_2O$ (**III**). A solution of *o*-(diphenylphosphino)benzaldehyde (0.96 g, 3.33 mmol) and 1,3-diaminopropane (0.14 cm^3, 1.67 mmol) in absolute ethanol (30 cm^3) was refluxed for 4 h. After cooling to room temperature, the yellow solution was transferred to a solution of $RuCl_2(DMSO)_4$ (0.82 g, 0.17 mmol) in absolute ethanol (10 cm^3) and then refluxed for another 16 h. The solvent of the resulting red solution was removed *in vacuo* to give a red residue. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on a silica gel column (2 × 15 cm). A red band was obtained when the column was eluted with CH_2Cl_2. The solvent of the red band was concentrated to *ca* 10 cm^3. Diethyl ether was then added to the CH_2Cl_2 solution until it just turned cloudy. The CH_2Cl_2/diethyl ether mixture was then cooled to −20°C to give orange crystals, which were filtered and dried *in vacuo*. Yield: 0.88 g, 67%, m.p. 312–313°C. Found: C, 59.8; H, 4.7; N, 3.4; Cl, 8.6. Calc. for $(C_{41}H_{36}N_2P_2Cl_2Ru)\cdot 2H_2O$: C, 59.6; H, 4.8; N, 3.4; Cl, 8.6%. IR (cm^{-1}, in KBr): 3470br, 3052m, 2960w, 2922w, 1631s, 1482s, 1432s, 1260m, 1094s, 805s, 744s, 694vs. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 64.9 (s) ^1H NMR ($CDCl_3$): δ 1.56 (4H, s, H_2O), 3.65 (2H, m, —NCH_2 CH_2CH_2N—), 4.23 (4H, t, *J* = 7.6 Hz, —HCH_2 CH$_2$CH_2N—), 6.93–7.61 (28H, m, Ph-*H*), 9.02 (2H, d, *J* = 8.4 Hz, —C*H*=N—). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$): δ 33.4 (s, —NCH$_2$*C*H$_2$CH$_2$N—), 65.6 (s, —N*C*H$_2$CH$_2$*C*H$_2$N—), 120.1–141.4 (m, Ph-*C*), 166.8 (s, —*C*H=N—). LRMS (FAB: +ve) *m/z*: 791 [M+1].

(*iv*) *Trans*-$RuCl_2(P_2N_2H_4)$ (**IV**). A suspension of $RuCl_2(DMSO)_4$ (0.29 g, 0.60 mmol) and $P_2N_2H_4$ (0.36 g, 0.60 mmol) in toluene (30 cm^3) was refluxed

for 48 h. The resulting orange solution was cooled to room temperature and filtered. The orange filtrate was concentrated to *ca* 10 cm^3 and cooled to −20°C to give yellow crystals which were filtered and dried *in vacuo*. Yield: 0.33 g, 70%, m.p. 305–307°C. Found: C, 61.4; H, 4.9; N, 3.6; Cl, 8.9. Calc. for $C_{40}H_{38}N_2P_2Cl_2Ru$: C, 61.5; H, 4.9; N, 3.6; Cl, 9.0%. IR (cm^{-1}, in KBr): 3200s, 3040s, 2910m, 2890m, 1520m, 1430s, 1380vs, 1285w, 1064m, 900w, 720m, 530vs. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 45.9 (s). ^1H NMR ($CDCl_3$): δ 3.07 (2H, m, —N*H*—), 3.32 (2H, m) and 3.78 (2H, m), —NCH_2CH_2N—, 4.57 (2H, m) and 4.84 (2H, m) (PhCH_2—); 6.96–7.29 (28H, m, Ph-*H*). $^{13}C-\{^1H\}$ NMR ($CDCl_3$): δ 5.15 (s, —NCH$_2$CH$_2$N—), 56.7 (s, PhCH$_2$—), 126.8–140.8 (m, Ph-*C*). LRMS (FAB: +ve) *m/z*: 781 [M+1].

(*v*) *Trans*-$RuCl_2(P_2N_2C_2$-amide) (**V**). A suspension of $RuCl_2(DMSO)_4$ (0.29 g, 0.60 mmol) and $P_2N_2C_2$-amide (0.38 g, 0.60 mmol) in toluene (30 cm^3) was refluxed for 20 h. The resulting orange solution was cooled to room temperature and filtered. The orange filtrate was concentrated to *ca* 10 cm^3 and cooled to −20°C to give orange crystals which were filtered and dried *in vacuo*. Yield: 0.28 g, 59%, m.p. 208–230°C (dec.). Found: C, 59.2; H, 4.3; N, 3.4; Cl, 8.6. Calc. for $C_{40}H_{34}O_2N_2P_2Cl_2Ru$: C, 59.4; H, 4.2; N, 3.5; Cl, 8.8%. IR (cm^{-1}, in KBr): 3327s, 2928s, 2850m, 1624vs, 1600vs, 1575vs, 1539s, 1449w, 1436m, 1362w, 1312m, 1271w, 1244m, 1090m, 1018w, 694w, 641w, 530w, 510w. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 48.1 (s). ^1H NMR ($CDCl_3$): δ 4.25 (4H, s, —NCH_2CH_2N—), 6.85–7.75 (28H, m, Ph-*H*), 8.89 (2H, s, —CON*H*—). $^{13}C-\{^1H\}$ NMR ($CDCl_3$): δ 68.2 (s, —NCH$_2$CH$_2$N—), 127.0–134.8 (m, Ph-*C*), 171.4 (s, —*C*ONH—). LRMS (FAB: +ve) *m/z*: 809 [M+1].

Preparation of iron (2+) complexes

(*i*) *Trans*-$[Fe(P_2N_2C_2)(CH_3CN)_2](ClO_4)_2$ (**VI**). A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.44 g, 1.2 mmol) and $P_2N_2C_2$ (0.73 g, 1.2 mmol) in acetonitrile (40 cm^3) was refluxed for 12 h. A deep red solution was obtained. The solution was concentrated *in vacuo* to *ca* 20 cm^3, then diethyl ether (20 cm^3) was added to the concentrated solution to give red solids which were filtered. The red solid was redissolved in a minimum amount of acetonitrile. Diethyl ether was added to the acetonitrile solution slowly until it just turned cloudy. The acetonitrile/diethyl ether mixture was then cooled to −20°C to give dark red crystals, which were filtered and dried *in vacuo*. Yield: 0.99 g, 87%, m.p. 195–196°C. Found: C, 56.1; H, 4.4; N, 6.1. Calc. for $C_{44}H_{40}N_4O_8Cl_2P_2Fe$: C, 56.1; H, 4.3; N, 6.0%. IR (cm^{-1}, in KBr): 3050w, 2945m, 2900m, 2480s, 1625s, 1479s, 1435s, 1176m, 1030vs, 748m, 694vs, 622m, 494s. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 53.6 (s). ^1H NMR ($CDCl_3$): δ 9.50 (2H, s, —C*H*=N—), 6.67–8.10 (28H, m, Ph-*H*), 4.41 (4H, s, —NCH_2CH_2N—), 1.83 (6H, s, CH_3CN).

(*ii*) *Trans*-$[Fe(P_2N_2C_2H_4)(CH_3CN)_2](ClO_4)_2$ (**VII**). A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.30 g, 0.83 mmol) and $P_2N_2C_2H_4$ (0.51 g, 0.83 mmol) in acetonitrile (40 cm^3) was refluxed for 18 h. An orange solution was obtained. The solution was concentrated *in vacuo* to *ca* 20 cm^3, then diethyl either (20 cm^3) was added to give orange red solids which were filtered. The orange red solid was redissolved in a minimum amount of acetone and chromatographed on a silica gel column (2×15 cm). An orange band was obtained when eluted with acetone. The solvent of the orange band was removed *in vacuo*, the residue redissolved in *ca* 10 cm^3 of acetonitrile and then diethyl ether was added until the solution just turned cloudy. The acetonitrile/diethyl ether mixture was then cooled to −20°C to give orange red crystals, which were filtered and dried *in vacuo*. Yield: 0.48 g, 61%, m.p. 243–245°C. Found: C, 56.1; H, 4.8; N, 6.0. Calc. for $C_{44}H_{44}N_4O_8Cl_2P_2Fe$: C, 55.9; H, 4.7; N, 5.9%. IR (cm^{-1}, in KBr): 3403w, 3010m, 2920w, 2476s, 1600s, 1565vs, 1480m, 1432m, 1031vs, 694vs. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 51.4 (s). ^1H NMR ($CDCl_3$): δ 7.29–7.84 (28 H, m, Ph-*H*); 5.02 (2H, m) and 4.93 (2H, m) (PhCH_2—); 4.12 (2H, m) and 3.67 (2H, m) (—NCH_2CH_2N—); 3.42 (2H, m, —N*H*—), 1.94 (6H, s, CH_3CN).

(*iii*) *Trans*-$FeCl_2(P_2N_2C_6)$ (**VIII**). A solution of $FeCl_2 \cdot 4H_2O$ (0.38 g, 1.9 mmol) and excess iron powder (0.5 g) in ethanol (30 cm^3) was refluxed for 2 h. The resulting solution was cooled and filtered into a solution of $P_2N_2C_6$ (1.25 g, 1.9 mmol) in ethanol (10 cm^3). The reaction mixture was then refluxed for 18 h to give an orange solution. The solvent was removed *in vacuo* to give an orange residue. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on a silica gel column (2×15 cm). A orange band was obtained when eluted with CH_2Cl_2. The solution was concentrated to *ca* 10 cm^3 and then hexane was added slowly until the solution just turned cloudy. The CH_2Cl_2/hexane mixture was cooled to −20°C to give orange crystals, which were filtered and dried *in vacuo*. Yield: 1.09 g, 73%. m.p, 258–260°C. Found: C, 66.9; H, 5.2; N, 3.5. Calc. for $C_{44}H_{42}N_2Cl_2P_2Fe$: C, 67.1; H, 5.3; N, 3.6%. IR (cm^{-1}, in KBr): 3048m, 2942m, 2820m, 1620vs, 1438vs, 735s, 708m. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 52.1 (s). ^1H NMR ($CDCl_3$): δ 9.24 (2H, d, J_{P-CH} = 5.4 Hz; —C*H*=N—), 7.23–8.38 (28H, m, Ph-*H*), 3.83 (4H,

t, J = 3.0 Hz; —NCH_2(CH_2)$_4$CH_2N—), 1.77 (4H, m, —NCH_2CH_2CH_2CH_2CH_2CH_2N—), 1.49 (4H, m, —NCH_2CH_2CH_2CH_2CH_2CH_2N—). LRMS (FAB: +ve) m/z: 788 [M+1].

Redox reactions of **II**

(*i*) *Oxidation.* Aqueous hydrogen peroxide (30% in H_2O_2, 1.0 cm^3) was added to a red solution of **II** (0.20 g, 0.25 mmol) in acetonitrile (30 cm^3) at room temperature. After stirring for 10 h, the colour of the solution changed from red to yellow. The solvent was removed *in vacuo* and the residue was then extracted with $CHCl_3$ (2 × 10 cm^3). The $CHCl_3$ extract was dried over $MgSO_4$, filtered and concentrated to *ca* 5 cm^3. Diethyl ether was then added to the $CHCl_3$ solution until it turned cloudy. The $CHCl_3$/diethyl ether mixture was then cooled to −20°C to give orange crystals which were filtered and dried *in vacuo*. The IR, LRMS, ^{1}H and ^{31}P NMR spectra of the orange crystals were identical to those of **V**. Yield: 0.12 g, 59%.

(*ii*) *Reduction.* A solution of **II** (0.15 g, 0.19 mmol) and $NaBH_4$ (0.10 g, 2.64 mmol) in ethanol (40 cm^3) was refluxed for 16 h. The solvent was removed *in vacuo* to give a brown residue. The brown residue was washed with water (2 × 10 cm^3) and extracted with CH_2Cl_2 (2 × 10 cm^3). The orange CH_2Cl_2 extract was dried over $MgSO_4$, filtered and concentrated to *ca* 5 cm^3. Diethyl ether was added to the orange CH_2Cl_2 extract until it turned cloudy. The CH_2Cl_2/diethyl ether mixture was cooled to −20°C to give orange crystals which were filtered and dried *in vacuo*. The IR, LRMS, ^{1}H and ^{31}P NMR spectra of the orange crystals were identical to those of **IV**. Yield: 0.11 g, 74%.

X-ray diffraction study

Yellow crystals of **IV** suitable for X-ray diffraction were grown from $CHCl_3$/diethyl ether as a solvate of stoichiometry **IV**·$CHCl_3$. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω–2θ scans at room temperature. The data were corrected for Lorentz, polarization effects and absorption correction using ψ-scan method. Crystal data, data collection parameters and results of the analysis are given in Table 3. The structure was solved by Patterson methods (SAPI) and refined by full-matrix least-squares techniques. All non-hydrogen and non-carbon atoms were refined anisotropically and all carbon atoms were refined isotropically. The hydrogen atoms were generated in their idealized positions (C—H = 0.96 Å) and included in structure factor calculations but not in the refinement. All calculations were performed on a Silicon-Graphics

Table 3. Data collection and processing parameters for **IV**

Molecular formula	$[C_{40}H_{34}N_2P_2Cl_2Ru]\cdot CHCl_3$
Molecular weight	896.02
Colour and habit	Yellow blocks
Unit cell parameters	a = 10.923 (4) Å
	b = 15.795 (4) Å
	c = 23.522 (4) Å
	β = 97.86 (2) Å
	V = 4020 (1) Å^3
	Z = 4
Density (calcd) (g cm^{-3})	1.480
Space group	$P2_1/n$ (no. 14)
Absorption coefficient (cm^{-1})	8.34
Crystal size (mm^3)	0.24 × 0.28 × 0.34
Scan type and rate (°mm^{-1})	ω–2θ; 16.0 up to 4 scans
Scan range	1.00+0.35 tan θ
Collection range	$4 \leqslant 2\theta \leqslant 45$
Unique data measured	5482
Observed data with $I > 3\sigma(I)$, n	1998
Number of variables, p	240
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.072
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma w \|F_o\|^2]^{1/2}$	0.081
Weighting scheme	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.018F_o^2]^2$
$S = \Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	1.87
Residual extrema in final difference map (eÅ^{-3})	1.23 to −0.91

computer using the program package teXan[18] from MSC. The relatively high R values are due to poor crystal quality and also thermal disorder of the phenyl rings.

Catalytic studies

Catalytic experiments were carried out in a 200-cm^3 stainless autoclave (model GCF-0.2) equipped with a glass liner, a stirrer and a temperature control unit. The solvent, catalyst and acrylic acid were transferred to the autoclave via the glass liner. The autoclave was flushed with hydrogen three times by pressurizing the autoclave to the desired pressure for 30 s before releasing the pressure. After the autoclave was thoroughly flushed with hydrogen, the autoclave was pressurized to the desired hydrogen pressure, stirred at a rate of 500 rpm and quickly raised to the desired temperature. The solution in the autoclave was allowed to react at the desired temperature for 1.5 h before it was cooled to room temperature. Then the pressure of the autoclave was released slowly and the reaction mixture was analysed by gas chromatography (packing: 10% polyethyleneglycol succinate on Chromosorb W, 60–80 mesh, 2M).

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